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The Progress of Oxidation in the Milk Powder Granule

GEORGE R. GREENBANK

&

MICHAEL J. PALLANSCH

Dairy Products Laboratory,
Eastern Utilization Research and Development Division,
Agricultural Research Service, U.S. Department of Agriculture,
Washington 25, D.C., USA

A large fraction of the fat in dried whole milk is encapsulated and resists simple solvent extraction. That fraction of the fat which can be easily extracted has been called "free" fat by Holm and Greenbank (3) who first observed this feature. These investigators also noted that homogenization of the milk prior to spray drying increased the product's storage stability. The increased shelf life was thought to result from a better coverage of the fat globules by the dry milk solids.

A relatively high free fat was found to occur in a new type of whole milk powder made in the laboratories of the Eastern Utilization Research and Development Division by the vacuum drying of a milk foam (5). Since this powder was also subject to rapid deterioration during storage in air, the preferential susceptibility of the "free" fat to oxidation was determined.

MATERIALS AND METHODS

Production and Storage of Milk Powder Samples

Fresh, morning milk obtained from the Beltsville Experiment Station was standardized to 3.3% fat, condensed to 50% solids, homogenized at 4500 p.s.i. and dried as described by Sinnamon, Aceto, Eskew and Schoppet (5). The powders were stored in air at 40°F. Samples were taken at regular intervals for flavor evaluation and chemical analysis.

Extraction of Lipid Fractions

Prior to chemical analysis it was essential that a method be developed to isolate the different fractions; this is described in the following paragraphs.

"Free glycerides" (FG), a fraction equivalent to the classic "free fat", were extracted by mixing 175 grams of powder with 600 ml of CCl_4 in a modified Waring Blendor (2) for one-half hour using a speed of 500 r.p.m. The solvent was filtered free of solids and the FG fraction was obtained by evaporation of the solvent at reduced temperature with a high vacuum pump and a dry ice solvent trap. Chemical analysis showed no phosphorous in this material.

"Free lipids" (FL), a fraction containing both the easily available triglycerides and phosphatides, were obtained by following the procedure outlined for FG except that the solvent was 97.5% CCl_4 and 2-1/2% absolute ethyl alcohol.

Total glycerides (TG) in the powders were removed by slurring a 175-gram powder sample with 585 ml of CCl_4 in the Blendor at 500 r.p.m. After thorough mixing, 15 ml of H_2O were added dropwise while the mixing continued. Total mixing time was 30 minutes. The extraction procedure was then continued as above.

Total lipids (TL) in the samples of milk powder were extracted by slurring a mixture of 175 grams of powder, 570 ml CCl_4 and 15 ml absolute alcohol in a Blendor as indicated. After 10 minutes of stirring, 15 ml of H_2O was added dropwise while extraction continued. Total extraction time was held to 30 minutes. The TL fraction was recovered from the extract in a fashion similar to the above.

Determination of Peroxide Value (PV)

The peroxide in the isolated fractions was determined by using a variation of a previously described method (2) designed to overcome the known insensitivity of the technique (1). A small glass vial containing a weighed sample of fat was transferred into a 120 ml nitrogen filled Erlenmeyer flask. The fat was dissolved in 6.25 ml of acetic acid-chloroform mixture (2:1 v/v). A 0.25 ml portion of a saturated solution of KI was then added. After thorough mixing the flask was held in the dark for 1 minute and then 0.5 ml of a 4% starch solution was added. This was followed by 25 ml of a 5% sodium acetate solution. The mixture was thoroughly shaken and allowed to stand 1 minute for phase separation. The supernatant material was decanted into a colorimeter tube and centrifuged for 1 minute at 3000 r.p.m. in a clinical centrifuge. The optical density of the solution was determined using a Klett-Summerson colorimeter equipped with a 540 $\text{m}\mu$ filter. A fat free sample was used as the blank.

In some samples containing phosphatides a slight turbidity developed which could not be removed by centrifuging. In these instances the optical density was obtained by taking the initial colorimeter reading and subtracting from it a second reading obtained after decolorizing the sample with a drop of .1 N sodium thiosulfate.

The peroxide values were obtained from a standard curve prepared by measuring the iodine liberated from serially diluted samples of .002 N KIO_3 using the same conditions as described except that the KI must be added before the KIO_3 . The standard curve in which the optical density (O.D.) is plotted against PV (meq. peroxide/kg. fat) is linear, passes through the origin and has a slope of .025.

Determination of Thiobarbituric Acid Value (TBAV)

The extent of oxidative change in the various fat fractions was further evaluated by determining the concentration of recognized oxidation products in the material.

This was done using a method described by Sidwell, Salwin and Mitchell (4) in which the intensity of the red color produced on heating solutions containing thiobarbituric acid and oxidation products is observed.

A standard curve for the reaction was prepared by forming known amounts of malonic dialdehyde in the reaction system by the action of acid on 1, 1, 3, 3-tetraethoxypropane (TEP). Ten ml volumetric flasks containing varying amounts of a 10^{-5} molar solution of TEP were brought up to volume with a .34% solution of TBA in 50% acetic acid, heated for 70 minutes at 100°C and cooled. The optical density of the solution was determined using a Klett-Summerson colorimeter equipped with a $540\text{ m}\mu$ filter. The color produced in the system containing 1 ml of a 10^{-5} M TEP solution was taken as equivalent to 1000 TBAV units. The standard curve obtained was linear, passed through the origin and had a slope of .16 O.D./TBAV units/g.

Flavor Evaluation

The flavor quality of the milk powder under investigation was determined by reconstituting the samples to 13% solids, holding overnight in a refrigerator and submitting them to the judgment of a ten man "expert" type taste panel. The samples were scored in accordance with a modified American Dairy Science Association score card. For comparison purposes, fresh market milk has an average score of 37 when submitted to this panel.

RESULTS

In all powders investigated, oxidation was found to occur rapidly in those lipid fractions most accessible to solvent extraction. Both the PV and the TBAV were higher in the FG and FL fractions than in the TG and TL fractions.

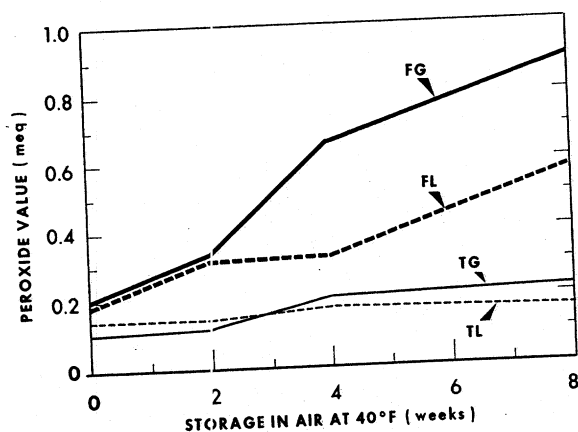


Figure 1. A comparison of the change in the peroxide value of the four lipid fractions of a powder during storage at 40°F .

Figure 1 demonstrates the change in the PV of the four lipid fractions of a typical milk powder during 8 weeks of storage in air at 40°F. The FL and TL fractions containing the oxidation sensitive phosphatides were found to contain less peroxide than the comparative glyceride fractions.

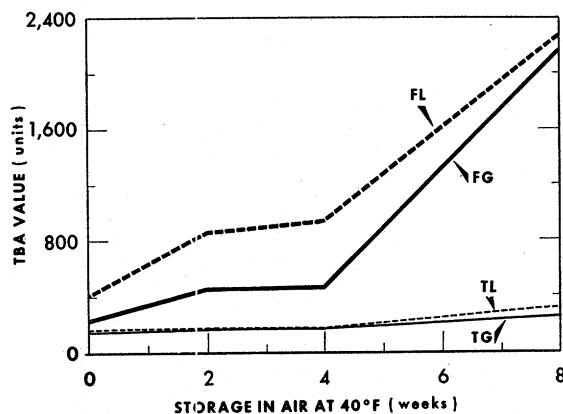


Figure 2. The change in the TBA value of the four lipid fractions during storage.

Typical TBAV for the four lipid fractions are shown in Figure 2. From this it can be seen that those fractions containing phosphatides material show higher concentrations of oxidative end products.

In all cases an increase in oxidative change in the fractions most accessible to solvent extraction was associated with a decrease in flavor score. Figure 3 shows the relationship between the change in TBAV in the FL fractions isolated from powders of relatively good and poor keeping quality and the change in their flavor score.

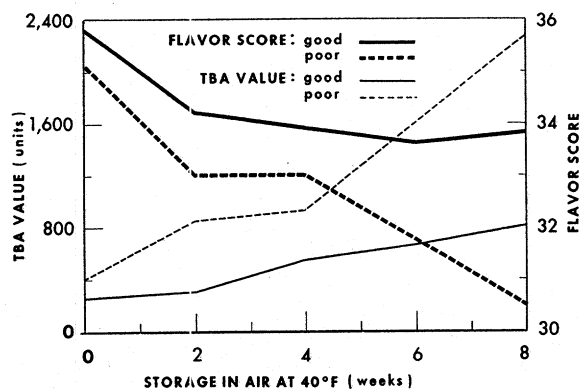


Figure 3. The change in the TBA value and flavor score of the free lipids of a good and poor keeping quality powder during storage.

DISCUSSION

The data obtained in this investigation substantiate the idea that oxidation of the milk lipids proceeds preferentially in those fractions most accessible to solvent extraction.

Oxidized flavor in dairy products is generally believed to be caused by aldehydes and other oxidation products. Figure 2 shows that the aldehydes (TBAV) of the fractions containing phosphatides (FL and TL) are usually higher than those where they are absent. These differences are small but when it is considered that the phosphatide concentration is low (approx. 0.7%) the differences become more significant.

The data reported in this paper also indicate that the PV of the FG fraction or the TBAV of the FL fraction is a much more sensitive indicator of oxidative change in the milk powders than similar analyses performed on the TL fraction.

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George R. Greenbank & Michael J. Pallansch,
Dairy Products Laboratory,
Eastern Utilization Research and Development Division,
Agricultural Research Service, U.S. Department of Agriculture,
Washington 25, D.C., USA

SUMMARY

Methods have been developed to separate the fat of whole milk powder into four fractions as follows: (1) free glycerides usually called free fat; (2) free lipids composed of the free glycerides and free phosphatides; (3) total glycerides; (4) total lipids composed of the total glycerides and total phosphatides. Puff-dried whole milk was stored in air at 40°F. Samples were removed at different time intervals and the four fractions separated. An aliquot was reconstituted and scored by a trained panel. The free glycerides and free lipids began to oxidize 2 to 4 weeks before the total glycerides and lipids. As a rule, the TBA value of the fractions containing phosphatides was higher than those without, whereas the peroxide

value was lower. The peroxide value of the free glycerides and lipids was always higher than that of the total glycerides and lipids, and also higher in a relatively poor-keeping-quality powder than in a good sample. The score decreases with increased TBA value.

Evolution de l'oxydation dans le lait en poudre

George R. Greenbank & Michael J. Pallansch,
Dairy Products Laboratory,
Eastern Utilization Research and Development Division,
Agricultural Research Service, U.S. Department of Agriculture,
Washington 25, D.C., USA

RESUME

On a développé des méthodes de séparation de la matière grasse du lait entier en poudre en quatre fractions comme suit : (1) glycérides libres généralement désignés par matière grasse libre ; (2) lipides libres constitués des glycérides libres et des phosphatides libres ; (3) glycérides totaux ; (4) lipides totaux comprenant les glycérides totaux et les phosphatides totaux. Le lait entier préparé par pulvérisation a été conservé à 40°F (4,4°C). Des échantillons ont été prélevés à différents intervalles de temps et les quatre fractions séparées et jugées. Les glycérides et les lipides libres ont commencé à s'oxyder de 2 à 4 semaines avant les glycérides et les lipides totaux. En règle générale, le test TBA a donné des valeurs plus élevées pour les fractions contenant des phosphatides que pour celles n'en contenant pas, alors que les valeurs de l'indice de peroxyde étaient plus basses. L'indice de peroxyde des glycérides et des lipides libres a toujours été plus élevé que celui des glycérides et des lipides totaux. Il est également plus élevé pour une poudre de conservation relativement mauvaise que pour un échantillon de bonne qualité. La qualité diminue lorsque l'indice de TBA augmente.

Das Fortschreiten der Oxydation in Milchpulverkörnchen

George R. Greenbank & Michael J. Pallansch,
Dairy Products Laboratory,
Eastern Utilization Research and Development Division,
Agricultural Research Service, U.S. Department of Agriculture,
Washington 25, D.C., USA

ZUSAMMENFASSUNG

Man hat Methoden entwickelt, um das Fett in Vollmilchpulver in vier Teile zu zerlegen, nämlich: (1) Freie Glyceride, auch freies Fett genannt; (2) freie Lipiden, bestehend aus freiem Glyceriden und freien Phosphatiden; (3) Gesamtglyceride; (4) Gesamtlipide, bestehend aus Gesamtglyceriden und Gesamt-Phosphatiden. Zerstäubungs-Vollmilchpulver wurde in Luft von 40 Grad Fahrenheit gelagert. Zu verschiedenen Zeitintervallen wurden Muster gezogen und die Zerlegung in die

vier Teile vorgenommen. Ein aliquoter Teil wurde wieder aufgelöst und von einer Gruppe von Fachleuten beurteilt. Die freien Glyceride und die freien Lipide begannen 2 bis 4 Wochen vor den Gesamtglyceriden und -Lipiden zu oxydieren. Im allgemeinen war der TBA-Wert der Phosphatide enthaltenden Teile höher als der keine solchen enthaltenden, während der Peroxydwert niedriger war. Der Peroxydwert der freien Glyceride und Lipide war stets höher als der der Gesamtglyceride und -Lipide und ebenfalls höher in einem wenig haltbaren Pulver als in einem Muster guter Qualität. Mit erhöhtem TBA-Wert nimmt die Erfolgsziffer ab.

Oxydationens fremskriden i mælkpulverpartiklerne

George R. Greenbank & Michael J. Pallansch,
Dairy Products Laboratory,
Eastern Utilization Research and Development Division,
Agricultural Research Service, U.S. Department of Agriculture,
Washington 25, D.C., USA

SAMMENDRAG

Der er udviklet metoder til at adskille fedtet i sødmælkspulver i fire fraktioner, som følger: (1) frie glycerider, sædvanligvis kaldet frit fedt; (2) frie lipider sammensat af de frie glycerider og frie fosfatider; (3) totale glycerider; (4) totale lipider sammensat af de totale glycerider og totale fosfatider.

»Puff«-tørret sødmælk blev opbevaret i luft ved 40°F. Prøver blev udtaget med forskellig tidsinterval og de fire fraktioner adskilt. En lignende prøve blev rekonstitueret og bedømt af fagfolk.

De frie glycerider og frie lipider begyndte at oxyderes 2—4 uger før de totale glycerider og lipider. Som regel var TBA-(thiobarbitursyre) værdien større for fraktionen med fosfatider end uden, hvorimod peroxyd-værdien var lavere. Peroxyd-værdien af de frie glycerider og lipider var altid højere end for de totale glycerider og lipider, og også højere i et relativt dårlig holdbart pulver end i en god prøve. Points ved bedømmelsen faldt med stigende TBA-værdi.